



TITLE:

# Preparation, Structure, and Reactivity of Functionalized Organosilicon Compounds (SYNTHETIC ORGANIC CHEMISTRY - Synthetic Design)

AUTHOR(S):

Tamao, Kohei; Kawachi, Atsushi

---

CITATION:

Tamao, Kohei ...[et al]. Preparation, Structure, and Reactivity of Functionalized Organosilicon Compounds (SYNTHETIC ORGANIC CHEMISTRY - Synthetic Design). ICR Annual Report 1996, 2: 34-35

ISSUE DATE:

1996-03

URL:

<http://hdl.handle.net/2433/65706>

RIGHT:

# Preparation, Structure, and Reactivity of Functionalized Organosilicon Compounds

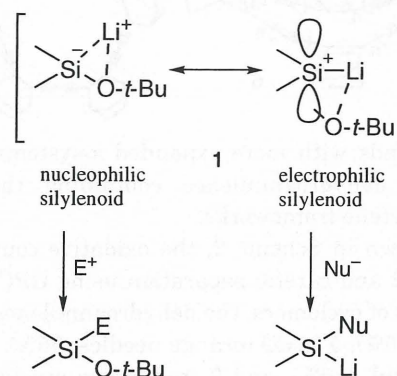
Kohei Tamao and Atsushi Kawachi

Preparation, structure, and reactivity of (alkoxysilyl)lithium, (alkoxy)oligosilanes, and pentacoordinate alkoxydisilane have been investigated. These functionalized organosilicon compounds containing a heteroatom substituents exhibit remarkable reactivities compared to ordinary organosilicon compounds.

**Keywords:** (Alkoxysilyl)lithium / Silylenoid / (Alkoxy)oligosilane / Skeletal rearrangement / Silylene / Pentacoordinate disilane / Thermal degradation

## (1) The Chemistry of Silylenoids: Preparation and Reactivity of (Alkoxysilyl)lithium [1]

We report the first results of silylenoid chemistry, analogous to carbenoid chemistry. (*t*-Butoxysilyl)lithium (*t*-BuO)Ph<sub>2</sub>SiLi (**1**) prepared from (*t*-butoxysilyl)stannane with *n*-BuLi in THF is stable at -78 °C. In the presence of 12-crown-4, **1** is stable as silyl anion even at 0 °C and reacts with electrophiles only. In contrast to this, **1** exhibits the ambiphilic reactivity and undergoes at 0 °C self-condensation smoothly to form (*t*-BuO)Ph<sub>2</sub>SiPh<sub>2</sub>SiLi or butylation in the presence of an excess amount of *n*-BuLi and TMEDA to form *n*-BuPh<sub>2</sub>SiLi. The ambiphilic reactivities of **1** could be accounted for by contribution of two extreme structures, that is, a nucleophilic silyl anionic structure and an electrophilic silylenoid structure. In the latter, the electropositive lithium atom bound to silicon ionizes and activates the silicon-oxygen bond so that the silicon becomes susceptible to the nucleophilic attack.



## (2) Palladium-Catalyzed Skeletal Rearrangement of (Alkoxy)oligosilanes via Silylene-Transfer [2]

Poly(alkoxy)trisilanes and tetrasilanes have been found to undergo clean skeletal rearrangement in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst at 80 - 140 °C in the fashion that the internal silylene moiety is transferred to the terminal positions. Ten substrates have

## SYNTHETIC ORGANIC CHEMISTRY — Synthetic Design —

### Scope of research

(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel  $\pi$ -conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfonium and episelenonium ions.



TAMAO TOSHIMITSU INOUE KAWACHI YAMAGUCHI

### Professor

TAMAO, Kohei (D Eng)

### Associate Professor

TOSHIMITSU, Akio (D Eng)

### Instructors

KAWACHI, Atsushi

YAMAGUCHI, Shigehiro

### Associate Instructor

INOUE, Yoshihiko (D Eng)

### Students

SUN, Guanri (Guest Scholar);

JIN, Ren-Zhi (Guest Scholar);

ASAHARA, Masahiro (DC);

TANAKA, Yoko (DC); NAKAMU-

RA, Kazunori (MC); MUKAI,

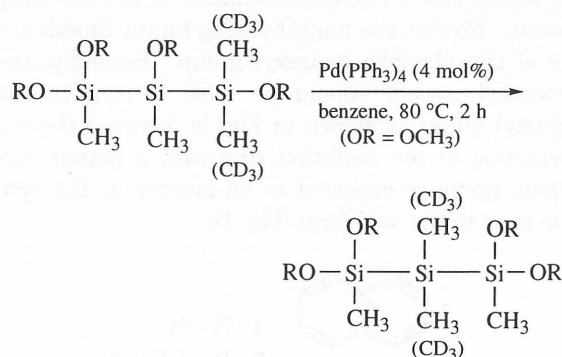
Takao (MC), OHNO, Shigeki (MC);

DOI, Noriyuki (MC); IIMURA,

(UG); TERADA, (UG)



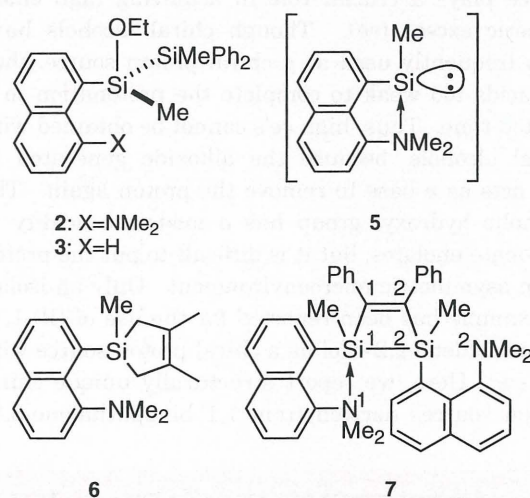
been examined. Typically, 1,2,2,3-(MeO)<sub>4</sub>Me<sub>4</sub>Si<sub>3</sub>, 1,1,2,3-(MeO)<sub>4</sub>Me<sub>4</sub>Si<sub>3</sub>, 1,2,3-(MeO)<sub>3</sub>Me<sub>5</sub>Si<sub>3</sub>, and 1,2-(MeO)<sub>2</sub>Me<sub>6</sub>Si<sub>3</sub>, are converted into the 1,1,1,3-, 1,1,3,3-, 1,1,3-, and 1,1-isomers, respectively, in quantitative yields: the reactivity decreases roughly in this order. In a deuterium-labeled study, 1,1,2,3-(MeO)<sub>4</sub>-3,3-(CD<sub>3</sub>)<sub>2</sub>Me<sub>2</sub>Si<sub>3</sub> gives 1,1,3,3-(MeO)<sub>4</sub>-2,2-(CD<sub>3</sub>)<sub>2</sub>-Me<sub>2</sub>Si<sub>3</sub> exclusively, no CD<sub>3</sub>/CH<sub>3</sub> random exchange being observed. A tetrasilane 1,2,3,4-(MeO)<sub>4</sub>Me<sub>6</sub>Si<sub>4</sub> is also transformed into the 1,1,4,4-isomer. A proposed mechanism involves silylene-transfer from the internal position to the terminal position(s) through the following key steps: oxidative addition of the Si-Si bond to Pd(0) and subsequent  $\alpha$ -elimination to a bis(silyl)(silylene)Pd complex, stabilized by the intramolecular coordination of alkoxy group(s) to the silylene center. The novel skeletal rearrangement may be useful for the structural modification of polyfunctionalized polysilanes of much current interest.



### (3) Remarkably Facile Thermal Generation of Silylene from a Pentacoordinate Alkoxydisilane and Its Trapping as a Pentacoordinate 1,2-Disilacyclobut-3-ene [3]

Pentacoordinate ethoxydisilane **2**, which contains the 8-dimethylamino-1-naphthyl group and the ethoxy group on the same silicon atom, and the tetra-coordinate counterpart **3** have been prepared. The X-ray structure analysis of **2** reveals that the geometry of the particular silicon atom is deformed from tetrahedral to pseudo-trigonal bipyramidal with the ethoxy group and the amino group at two pseudo-apical positions, having the N1...Si1 distance 2.969(3) Å and the N1...Si1-O1 angle 171.36(9)°. This compound has a normal Si1-Si2 distance 2.368(1) Å, a slightly

long Si-O bond 1.665(2) Å and a small O-Si-Si bond angle 97.35(8)°. The two methyl groups on nitrogen in **2** appear as diastereotopic two separate singlets in <sup>1</sup>H and <sup>13</sup>C NMR spectra at room temperature. **2** undergoes thermal degradation readily at 90°C in DMF or 110 °C in toluene to form EtOSiPh<sub>2</sub>Me (**4**) in high yields, while **2** is stable under similar conditions. The silylene species **5** is trapped efficiently with 2,3-dimethyl-1,3-butadiene and diphenylacetylene to form the corresponding adducts **6** and **7**, respectively. The X-ray structure analysis reveals that **7** is the first example of a pentacoordinate 1,2-disilacyclobut-3-ene and involves two different conformations of the 8-dimethylamino-1-naphthyl groups as shown below. The Si1 is highly pentacoordinated, with the N1...Si1 distance 2.789 (3) Å, while the N2...Si2 is long 3.039(3) Å, causing the 1,2-disilacyclobutene ring unsymmetrical with different bond lengths Si1-C1 1.932(3) Å and Si2-C2 1.891(3) Å. Compound **7** is oxygen-stable.



### References

1. Tamao K and Kawachi A, *Angew. Chem. Int. Ed. Engl.* **34**, 818 (1995).
2. Tamao K, Sun G-R and Kawachi A, *J. Am. Chem. Soc.* **117**, 8043 (1995).
3. Tamao K, Nagata K, Asahara M, Kawachi A, Ito Y and Shiro M, *J. Am. Chem. Soc.* **117**, 11592 (1995).